$\Delta C_p = C_{p,ZrO_2(\alpha)} - C_{p,Zr(\alpha)} - C_{p,O_2}$

Date. No.

6.1 $Zr(\alpha) + O_2 \rightarrow ZrO_2(\alpha) \quad \Delta H_{298} = -1100800\,J$

$298 \sim 1136K \Rightarrow \Delta C_p = 19.69 - 8.28\times10^{-3}T - 12.39\times10^{5}T^{-2}\ J/K$

$1136K \Rightarrow \Delta H_{trans} = 3900J,\ Zr(\alpha) \rightarrow Zr(\beta)$

$Zr(\beta) + O_2 \rightarrow ZrO_2(\alpha) \Rightarrow \Delta C_p = C_{p,ZrO_2(\alpha)} - C_{p,Zr(\beta)} - C_{p,O_2}$

$1136 \sim 1478K \Rightarrow \Delta C_p = 16.44 - 1.29\times10^{-3}T - 12.39\times10^{5}T^{-2}\ J/K$

$1478K \Rightarrow \Delta H_{trans} = 5900J,\ ZrO_2(\alpha) \rightarrow ZrO_2(\beta)$

$Zr(\beta) + O_2 = ZrO_2(\beta) \Rightarrow \Delta C_p = C_{p,ZrO_2(\beta)} - C_{p,Zr(\beta)} - C_{p,O_2}$

$1478 \sim 1600K \Rightarrow \Delta C_p = 21.3 - 8.82\times10^{-3}T + 1.67\times10^{5}T^{-2}\ J/K$

$$\Rightarrow \Delta H_{1600} = -1100800 + \int_{298}^{1136}(19.69 - 8.28\times10^{-3}T - 12.39\times10^{5}T^{-2})dT$$
$$+3900 + \int_{1136}^{1478}(16.44 - 1.29\times10^{-3}T - 12.39\times10^{5}T^{-2})dT$$
$$+5900 + \int_{1478}^{1600}(21.3 - 8.82\times10^{-3}T + 1.67\times10^{5}T^{-2})dT$$
$$= -1086000J = -1.086\times10^{6}J$$

$\Delta S_{298} = 50.4 - 205.1 - 39 = -193.7\,J/K$

$$\Delta S_{1600} = -193.7 + \int_{298}^{1136}\left(\frac{19.69 - 8.28\times10^{-3}T - 12.39\times10^{5}T^{-2}}{T}\right)dT$$
$$- \frac{3900}{1136} + \int_{1136}^{1478}\left(\frac{(16.44 - 1.29\times10^{-3}T - 12.39\times10^{5}T^{-2})}{T}\right)dT$$
$$+ \frac{5900}{1478} + \int_{1478}^{1600}\frac{(21.3 - 8.82\times10^{-3}T + 1.67\times10^{5}T^{-2})}{T}dT$$
$$= -118.6\,J/K$$

$H_{initial} = H_{product}$, $T = 2350K$

6.8 $\Delta H_{298} = -3 \times 910900 + 744800 = -1987900 J$

$\Delta S_{298} = 2 \times 191.5 + 3 \times 41.5 - 3 \times 205.1 - 113.0 = -220.8 J/K$

$\Delta C_p = 3C_{p,SiO_2(\alpha\text{-quartz})} + 2C_{p,N_2} - C_{p,Si_3N_4} - 3C_{p,O_2}$

$= 26.99 - 99.74 \times 10^{-3} T - 13.05 \times 10^5 T^{-2}$

$\Delta H_{800} = \Delta H_{298} + \int_{298}^{800} \Delta C_p dT$

$= -1987900 + 26.99(800 - 298) - \frac{99.74 \times 10^{-3}}{2}(800^2 - 298^2) + 13.05 \times 10^5 (\frac{1}{800} - \frac{1}{298})$

$= -2005000 J$

$\Delta S_{800} = -220.8 + \int_{298}^{800} \left(\frac{26.99 - 99.74 \times 10^{-3} T - 13.05 \times 10^5 T^{-2}}{T} \right) dT = -250.5 J/K$

$\Delta G_{800} = \Delta H_{800} - T\Delta S_{800} = -2005000 + 800 \times 250.5 = -1817000 J$

$\Delta C_p = 0$이라 가정

↳ $\Delta G_{800} = -1987900 + 800 \times 220.8 = -1811000 J$

오차 $= \frac{1817000 - 1811000}{1817000} = 0.33\%$

3. • 고전열역학적 방법

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S_{conf} = -k_B (n_A + n_B)\left[X_A \ln X_A + X_B \ln X_B\right]$$

$$\Delta S_{conf} = -KN\left\{\frac{n}{N}\ln\frac{n}{N} + \frac{N-n}{N}\ln\frac{N-n}{N}\right\}$$

$$\Delta G = n\cdot\Delta H_v + TK\left\{n\ln\frac{n}{N} + (N-n)\ln\left(\frac{N-n}{N}\right)\right\}$$

$$= n\cdot\Delta H_v + TK\left\{n\ln n - n\ln N + (N-n)\ln(N-n) - (N-n)\ln N\right\}$$

$$= n\cdot\Delta H_v + TK\left\{n\ln n - N\ln N + (N-n)\ln(N-n)\right\}$$

$$\frac{\partial\Delta G}{\partial n} = \Delta H_v + TK\left\{\ln n + 1 - \ln(N-n) - 1\right\}$$

$$= \Delta H_v + TK\cdot\left\{\ln\frac{n}{N-n}\right\} = 0$$

$$\frac{n}{N-n} = e^{-\frac{\Delta H_v}{KT}}$$

$$n\,e^{\frac{\Delta H_v}{KT}} = N-n$$

$$n\left(1+e^{\frac{\Delta H_v}{KT}}\right) = N$$

$$\Rightarrow \frac{n}{N} = \frac{1}{1+e^{\frac{\Delta H_v}{KT}}}$$

• 통계 열역학적 방법

$$\frac{n}{N} = \frac{e^{-\frac{\Delta H_v}{KT}}}{Z}$$

$$Z = \Sigma e^{-E_i/KT} = 1 + e^{-\frac{\Delta H_v}{KT}}$$

$$\frac{n}{N} = \frac{e^{-\frac{\Delta H_v}{KT}}}{1+e^{-\frac{\Delta H_v}{KT}}} = \frac{1}{1+e^{\frac{\Delta H_v}{KT}}}$$